

1      **BINDERS CONTAINING AN EPOXY RESIN, AN ESTER OF A FATTY ACID,**  
2                   **AND A FLUORINATED ACID**

4      **Field of the Invention**

5      This invention relates to foundry binder systems, which cure in the presence of sulfur  
6      dioxide and an oxidizing agent, comprising (a) an epoxy resin; (b) an ester of a fatty  
7      acid; (c) a fluorinated acid, preferably hydrofluoric acid; (d) an effective amount of a  
8      oxidizing agent; and (e) no ethylenically unsaturated monomer or polymer. The  
9      foundry binder systems are used for making foundry mixes. The foundry mixes are used  
10     to make foundry shapes (such as cores and molds) which are used to make metal  
11     castings, particularly ferrous castings.

12

13     **Description of the Related Art**

14     In the foundry industry, one of the procedures used for making metal parts is “sand  
15     casting”. In sand casting, disposable molds and cores are fabricated with a mixture of  
16     sand and an organic or inorganic binder. The foundry shapes are arranged in core/mold  
17     assembly, which results in a cavity into which molten metal will be poured. After the  
18     molten metal is poured into the assembly of molds and cores and cools, the metal part  
19     formed by the process is removed from the assembly. The binder is needed so the  
20     molds and cores will not disintegrate when they come into contact with the molten  
21     metal.

22

23     Two of the prominent fabrication processes used in sand casting are the no-bake and the  
24     cold-box processes. In the no-bake process, a liquid curing catalyst or co-reactant is  
25     mixed with an aggregate and binder to form a foundry mix before shaping the mixture  
26     in a pattern. The foundry mix is shaped by putting it into a pattern and allowing it to  
27     cure until it is self-supporting and can be handled. In the cold-box process, a gaseous  
28     curing catalyst or co-reactant is passed through a shaped mixture (usually in a corebox)  
29     of the aggregate and binder to cure the mixture.

30

1 A cold-box process widely used in the foundry industry for making cores and molds is  
2 the “SO<sub>2</sub> cured epoxy/acrylate system”. In this process, a mixture of a hydroperoxide  
3 (usually cumene hydroperoxide), an epoxy resin, a multifunctional acrylate, typically a  
4 coupling agent, and optional diluents, are mixed into an aggregate (sand) and  
5 compacted into a specific shape, typically a core or mold. Sulfur dioxide (SO<sub>2</sub>),  
6 optionally diluted with nitrogen or another inert gas, is blown into the binder/aggregate  
7 shape. The shape is instantaneously hardened and can be used immediately in a  
8 foundry core/mold system. In this binder system, the acrylate component must be kept  
9 separate from the hydroperoxide until the binder is applied to sand, otherwise, free  
10 radical polymerization of the acrylate component will begin prematurely and render the  
11 binder useless.

12  
13 German Patent Application DE 197 27 540 discloses examples of epoxy-acrylic  
14 foundry binders containing methyl-, ethyl- and propyl-esters of oleic acid, which are  
15 cured with sulfur dioxide in the presence of a free radical initiator.

16  
17 **Brief Summary of the Invention**

18  
19 The subject invention relates to foundry binder systems, which cure in the presence of  
20 gaseous sulfur dioxide and an oxidizing agent, comprising:

21  
22 (a) 45 to 80 parts by weight of an epoxy resin;

23  
24 (b) 5 to 40 parts of an ester of a fatty acid;

25  
26 (c) 0.05 to 3 parts of a fluorinated acid;

27  
28 (d) an effective amount of an oxidizing agent; and

29  
30 (e) 0 parts of an ethylenically unsaturated monomer or polymer.

1  
2 wherein (a), (b), (c), and (d) are separate components or mixed with another of  
3 said components, and where said parts by weight are based upon 100 parts of  
4 binder.

5  
6 It has been found that addition of the fluorinated acid to an acrylate-free binder provides  
7 foundry shapes that have better tensile strength development and humidity resistance  
8 than foundry shapes made with binders that do not contain the fluorinated acid. Tests  
9 have also shown that the foundry shapes, made with these binders, have better tensile  
10 strength development and humidity resistance than those made with similar binders  
11 containing an acrylate and no fluorinated acid. This is beneficial in the casting of both  
12 light metal (e.g. aluminum) and ferrous parts.

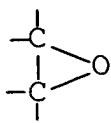
13  
14 Another advantage of the binder, because it is acrylate-free, is that all of the  
15 components of the binder can be sold and used in one package. This simplifies the  
16 customer's binder storage and handling operations.

17  
18 The foundry binders are used for making foundry mixes. The foundry mixes are used  
19 to make foundry shapes, such as cores and molds, which are used to make metal  
20 castings.

21  
22 **Detailed Description of the Invention**

23 The detailed description and examples will illustrate specific embodiments of the  
24 invention will enable one skilled in the art to practice the invention, including the best  
25 mode. It is contemplated that many equivalent embodiments of the invention will be  
26 operable besides these specifically disclosed. All percentages are percentages by  
27 weight unless otherwise specified.

28  
29 An epoxy resin is a resin having an epoxide group, i.e.,



such that the epoxide functionality of the epoxy resin (epoxide groups per molecule) is equal to or greater than 1.9, typically from 2.0 to 4.0.

Examples of epoxy resins include (1) diglycidyl ethers of bisphenol A, B, F, G and H, (2) halogen-substituted aliphatic epoxides and diglycidyl ethers of other bisphenol compounds such as bisphenol A,B, F, G, and H, and (3) epoxy novolacs, which are glycidyl ethers of phenolic-aldehyde novolacs, (4) cycloaliphatic epoxy resins, and (5) mixtures thereof.

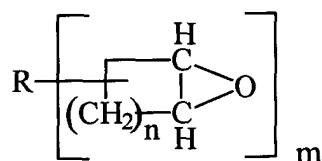
Epoxy resins (1) are made by reacting epichlorohydrin with the bisphenol compound in the presence of an alkaline catalyst. By controlling the operating conditions and varying the ratio of epichlorohydrin to bisphenol compound, products of different molecular weight can be made. Epoxy resins of the type described above based on various bisphenols are available from a wide variety of commercial sources.

Examples of epoxy resins (2) include halogen-substituted aliphatic epoxides, diglycidyl ethers of other bisphenol compounds such as bisphenol A, B, F, G, and H, and epoxy novolac resins. Examples of halogen-substituted aliphatic epoxides include epichlorohydrin, 4-chloro-1, 2-epoxybutane, 5-bromo-1,2-epoxypentane, 6-chloro-1,3-epoxyhexane and the like.

Examples of epoxy novolacs (3) include epoxy cresol and epoxy phenol novolacs, which are produced by reacting a novolac resin (usually formed by the reaction of orthocresol or phenol and formaldehyde) with epichlorohydrin, 4-chloro-1, 2-

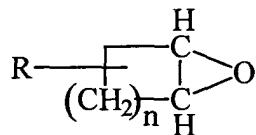
1 epoxybutane, 5-bromo-1,2-epoxypentane, 6-chloro-1, 3-epoxyhexane and the like.  
2  
3 Examples of cycloaliphatic epoxy resins include any aliphatic, cycloaliphatic, or mixed  
4 aliphatic-cycloaliphatic epoxide having any aliphatic groups, and further includes  
5 aliphatic epoxy resins having aromatic groups, i.e. mixed aliphatic-aromatic epoxy  
6 resins. The aliphatic epoxy resin may contain monomeric epoxide compounds in  
7 admixture with polymeric epoxide compounds. The most preferred aliphatic epoxy  
8 resins are represented by the following structural formulae:  
9  
10  
11

12 (I)



13  
14 where "n" ≥ 1 and "m" is a whole number, typically from 1 to 4, preferably from 2-3, or  
15  
16

17 (II)



18  
19 where "n" ≥ 1.  
20  
21 R in structures I and II is predominantly aliphatic in nature, but may contain oxygen  
22 functionality as well as mixed aliphatic-aromatic groups. Typically, R is selected from  
23 the group consisting of alkyl groups, cycloalkyl groups, mixed alkyl-cycloaliphatic  
24 groups, and substituted alkyl groups, cycloalkyl groups, or alkyl-cycloaliphatic groups,  
25  
26

1 where the substituents include, for example, ether, carbonyl, and carboxyl groups.

2

3 Specific examples of aliphatic epoxy resins include 3,4-epoxycyclohexylmethyl-3,4-  
4 epoxycyclohexane carboxylate; vinylcyclohexene dioxide; 2-(3,4-epoxycyclohexyl-5,5-  
5 spiro-3,4-epoxy) cyclohexane-meta-dioxane; bis-(3,4-epoxycyclohexyl) adipate; 1,2-  
6 epoxy-p-vinylcyclohexene; limonene dioxide; limonene monoxide; and hydrogenated  
7 bisphenol diglycidyl ethers.

8

9 Preferably used are epoxy resins having an average epoxide functionality of at least 2.1  
10 to 3.5, preferably from about 2.3 to about 3.0. Particularly preferred are epoxy resins  
11 having an average weight per epoxy group of 165 to 200 grams/equivalents.

12

13 Although it is contemplated that any esters of a fatty acid can be used in this invention,  
14 preferably used are esters of fatty acids where the fatty acid used to prepare the ester has  
15 a carbon chain of 12 carbon atoms or more, particularly 12-22 carbon atoms. Preferably  
16 the ester group of the ester of the fatty acid has 1 to 8 carbon atoms. The esters of the  
17 fatty acids can be readily prepared by transesterification of fats and oils of plant or  
18 animal origin, which are normally available in the form of triglycerides or can be  
19 prepared by esterification of fatty acids obtained from such fats and oils.

20

21 Rapeseed oil methyl ester is a typical example of an ester derived from plant oil; it is a  
22 suitable solvent, particularly since it is available at low cost in the form of diesel fuel.  
23 But the esters of other plant oils, such as soybean oil, linseed oil, sunflower oil, peanut  
24 oil, tung oil, palm kernel oil, coconut oil, castor oil and/or olive oil, can also be used. In  
25 addition, marine animal oil, tallow oil, and animal fats can also serve as starting  
26 materials for alkyl esters that are to be used according to this invention.

27

28 The oxidizing agent is a peroxide and/or hydroperoxide. Examples include ketone  
29 peroxides, peroxy ester free radical initiators, alkyl oxides, chlorates, perchlorates, and  
30 perbenzoates. Preferably, however, the free radical initiator is a hydroperoxide or a

1 mixture of peroxide and hydroperoxide. Hydroperoxides particularly preferred in the  
2 invention include t-butyl hydroperoxide, cumene hydroperoxide, paramenthane  
3 hydroperoxide, etc. The organic peroxides may be aromatic, aliphatic, or mixed  
4 aromatic-aliphatic peroxides.

5

6 Examples of useful diacyl peroxides include benzoyl peroxide, lauroyl peroxide and  
7 decanoyl peroxide. Examples of mixed aromatic-aliphatic and aliphatic peroxides  
8 respectively include dicumyl peroxide and di-t-butyl peroxide.

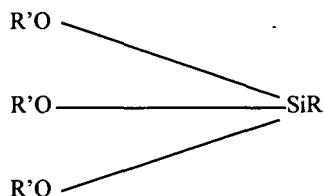
9

10 Solvents may also be added to the binder formulation. Typically, a solvent is used to  
11 reduce the viscosity of the binder, such that the resulting viscosity of the epoxy resin  
12 component is less than 1,000 centipoise, preferably less than 400 centipoise. Generally,  
13 the total amount of solvent is used in an amount of 0 to 25 weight percent based upon  
14 the total weight of the epoxy resin. Solvents that can be used include polar solvents,  
15 such as liquid dialkyl esters, e.g. dialkyl phthalate of the type disclosed in U.S. Patent  
16 3,905,934, and other dialkyl esters such as dimethyl glutarate, dimethyl succinate,  
17 dimethyl adipate, and mixtures thereof. Suitable aromatic solvents are benzene, toluene,  
18 xylene, ethylbenzene, and mixtures thereof. Preferred aromatic solvents are mixed  
19 solvents that have an aromatic content of at least 90% and a boiling point range of  
20 138°C to 232°C. Suitable aliphatic solvents include kerosene.

21

22 The binder may also contain a silane coupling agent having the following general  
23 formula:

24



25

26 wherein R' is a hydrocarbon radical and preferably an alkyl radical of 1 to 6 carbon  
27 atoms and R is an alkyl radical, an alkoxy-substituted alkyl radical, or an alkyl-amine-

1 substituted alkyl radical in which the alkyl groups have from 1 to 6 carbon atoms. The  
2 silane is preferably added to the binder in amounts of 0.01 to 2 weight percent,  
3 preferably 0.1 to 0.5 weight percent based on the weight of the binder.

4

5 Polyols such as phenolic resins, polyester resins, amine polyols, polyester polyols, and  
6 polyether polyols can also be used in the foundry binder.

7

8 Phenolic resins include phenolic resole resins, particularly benzylic ether phenolic  
9 resole resins, including alkoxy-modified benzylic ether phenolic resole resins. Benzylic  
10 ether phenolic resole resins, or alkoxyLATED versions thereof, are well known in the art,  
11 and are specifically described in U.S. Patent 3,485,797 and 4,546,124.

12

13 Polyether polyols are prepared by reacting an alkylene oxide with a polyhydric alcohol  
14 in the presence of an appropriate catalyst such as sodium methoxide according to  
15 methods well known in the art.

16

17 The polyester polyols may be aliphatic and/or aromatic polyester polyols. These  
18 polyols generally having a hydroxyl number from about 200 to 2,000, preferably from  
19 700 to 1200, and most preferably from 250 to 600 mg KOH/g.

20

21 The binder contains a fluorinated acid. Examples of fluorinated acids include  
22 hydrofluoric acid, ammonium fluoride, tris-hydrofluoric acid, ammoniumbifluoride,  
23 potassiumbifluoride, tetrafluoroboric acid, hexafluorophosphoric acid, hexafluorosilicic  
24 acid, N,N-diisopropyl-amine-tris (hydrogenfluoride), and N,N'-dimethyl-2-  
25 imidazolidone-hexakis(hydrogenfluoride). Preferably, the fluorinated acid is  
26 hydrofluoric acid, most preferably an aqueous solution of hydrofluoric acid, containing  
27 from 10 to 90 weight percent water, preferably 30 to 60 weight percent water.

28

29 The components of the binder can be combined as one component and added to the  
30 foundry aggregate, or can be added separately or in various combinations.

1  
2  
3 It will be apparent to those skilled in the art that other additives such as silanes,  
4 silicones, release agents, defoamers, wetting agents, etc. can be added to the aggregate,  
5 or foundry mix. The particular additives chosen will depend upon the specific purposes  
6 of the formulator.

7  
8 Typically, the amounts of the components used in the binder system are from 45 to 80  
9 parts by weight of epoxy resin, preferably from 50 to 70 parts by weight; from 5 to 40  
10 parts by weight of an ester of a fatty acid, preferably from 15 to 30 parts by weight;  
11 from 0.05 to 3 parts by weight of a fluorinated acid, preferably from 0.05 to 1.0 parts by  
12 weight; and from 10 to 40 parts by weight of oxidizing agent, preferably from parts by  
13 weight, wherein the weight percents are based upon 100 parts of the binder system.

14  
15 Various types of aggregate and amounts of binder are used to prepare foundry mixes by  
16 methods well known in the art. Ordinary shapes, shapes for precision casting, and  
17 refractory shapes can be prepared by using the binder systems and proper aggregate.  
18 The amount of binder and the type of aggregate used are known to those skilled in the  
19 art. The preferred aggregate employed for preparing foundry mixes is sand wherein at  
20 least about 70 weight percent, and preferably at least about 85 weight percent, of the  
21 sand is silica. Other suitable aggregate materials for ordinary foundry shapes include  
22 zircon, olivine, aluminosilicate, chromite sands, and the like.

23  
24 In ordinary sand type foundry applications, the amount of binder is generally no greater  
25 than about 10% by weight and frequently within the range of about 0.5% to about 7%  
26 by weight based upon the weight of the aggregate. Most often, the binder content for  
27 ordinary sand foundry shapes ranges from about 0.6% to about 5% by weight based  
28 upon the weight of the aggregate in ordinary sand-type foundry shapes.

29  
30 The foundry mix is molded into the desired shape by ramming, blowing, or other

1 known foundry core and mold making methods. The shape is then cured almost  
2 instantaneously by the cold-box process, using vaporous sulfur dioxide as the curing  
3 agent (most typically a blend of nitrogen, as a carrier, and sulfur dioxide containing  
4 from 35 weight percent to 65 weight percent sulfur dioxide), described in U.S. Patent  
5 4,526,219 and 4,518,723, which are hereby incorporated by reference. The shaped  
6 article is preferably exposed to effective catalytic amounts of gaseous sulfur dioxide,  
7 and, optionally, a carrier gas can be used. The exposure time of the sand mix to the gas  
8 is typically from 0.5 to 10 seconds. The foundry shape is cured after gassing with  
9 sulfur dioxide. Oven drying may be needed if the foundry shape is coated with a  
10 refractory coating.

11

12 The core and/or mold may be formed into an assembly. When making castings, the  
13 assembly may be coated with a water-based refractory coating and passed through a  
14 conventional or microwave oven to remove the water from the coating.

15

#### 16                           **ABBREVIATIONS**

17 The abbreviations used in the examples are as follows:

18

19       SCA                           silane coupling agent.

20

21       BT                           butyl ester of tall oil fatty acid, PLASTHALL 503 from  
22                                   CP Hall.

23

24       CHP                           cumene hydroperoxide.

25

26       ERL-4221                   an aliphatic epoxy resin, 3,4-epoxycyclohexylmethyl 3,4-  
27                                   epoxy-cyclohexane- carboxylate, manufactured by Union  
28                                   Carbide.

29

30       HF                           as a 49 weight percent aqueous solution.

1  
2 TONE 0301 caprolactone based trifunctional polyol with average  
3 molecular weight of 300 and a hydroxyl number of 560  
4 mg KOH/g, manufactured by Union Carbide.  
5

6 **EXAMPLES**

7 While the invention has been described with reference to a preferred embodiment, those  
8 skilled in the art will understand that various changes may be made and equivalents  
9 may be substituted for elements thereof without departing from the scope of the  
10 invention. In addition, many modifications may be made to adapt a particular situation  
11 or material to the teachings of the invention without departing from the essential scope  
12 thereof. Therefore, it is intended that the invention not be limited to the particular  
13 embodiment disclosed as the best mode contemplated for carrying out this invention,  
14 but that the invention will include all embodiments falling within the scope of the  
15 appended claims. In this application, all units are in the metric system and all amounts  
16 and percentages are by weight, unless otherwise expressly indicated.

17

18 **Testing Protocol**

19 The various formulations given in the following examples were evaluated by preparing  
20 test cores whose tensile strengths were measured over various times. How well a binder  
21 system bonds the particles of an aggregate (e.g. sand) together is typically evaluated by  
22 using tensile strength measurements given in pounds per square inch (psi). Sufficient  
23 core strength is needed once the binder/sand mix is cured to prevent the core/mold from  
24 distorting or cracking during assembly operations. Tensile strength measurements are  
25 taken immediately (20 seconds after core box opens), 5-minutes, one-hour, 24-hours  
26 and 24 hours at 90% relative humidity according to the standard ASTM sand tensile  
27 test. Cores made with binder systems that retain higher tensile strengths over time can  
28 better retain their dimensional accuracy and have less core breakage problems.

29  
30

## Comparison Example A

A binder, having no acrylic component or HF, was used in this comparison example.

The composition of the binder follows:

ERL 4221	57.57%
Butyl Tallate	27.21
CHP	15.02
SCA	0.20

10 A foundry mix was prepared by mixing 3000 grams of silica sand and 30 grams of the  
11 binder for 4 minutes using a Hobart sand mixer. The foundry mix was then blown into  
12 a three cavity tensile test specimen core box and gassed 0.5 second with a 65/35  
13 SO<sub>2</sub>/nitrogen mixture delivered by an MT Systems SO<sub>2</sub>/Nitrogen blending unit  
14 followed by a 10 second dry air purge. The tensile strengths were measured according  
15 to standard ASTM measurements and are summarized in Table I.

### Example 1

Comparison Example A was repeated using the following binder, which contained HF:

ERL 4221	57.5%
Butyl Tallate	27.18
CHP	15.0
SCA	0.20
HF	0.12

26 The tensile strengths were measured according to standard ASTM measurements and  
27 are summarized in Table I.

### Example 2

30 Example 1 was repeated using the following binder, which contained a polyol in

1 addition to HF:

2

3

4	ERL 4221	57.50%
5	TONE 0301	2.80
6	Butyl Tallate	24.38
7	CHP	16.50
8	SCA	0.20
9	HF	0.12

10 The tensile strengths were measured according to standard ASTM measurements and  
11 are summarized in Table I.

12

**Table I**

13 **(Test results related to tensile strengths of cores made with binders)**

Example	HF (pbw)	Polyol (pbw)	Tensile strengths of cores (psi)				
			Imm (20 sec)	5-min	1-hr	24 hrs	24 hr @ 95% RH
A	0	0	87	134	166	164	81
1	0.12	0	98	162	189	188	116
2	0.12	2.80	74	123	133	154	146

14

15 A comparison of Example A and Example 1 indicates that the addition of HF gives  
16 better sand tensile strengths, especially the 24-hour humidity resistance. Example 2  
17 indicates that the addition of HF and a polyol (TONE 0301) to the acrylate-free binder  
18 lowered the initial sand tensile strengths, but dramatically improved the humidity  
19 resistance by 80%, relative to the Comparison Example A.

20

21 Thus, the subject invention results in improvements that provide more flexibility to the

1 foundryman. Besides simplifying the customer's binder-storage and handling  
2 operations, improvements in tensile strength development allow use of lower binder  
3 levels. This provides benefits in the casting of metal parts from both aluminum and  
4 ferrous metals.

5

6